

[54] **PROCESS FOR PRODUCING
SUBSTITUTED-1-ACETYL-3,3-DIMETHYL-
CYCLOHEXANE**

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[21] Appl. No.: **753,453**

[22] Filed: **Dec. 22, 1976**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 713,429, Aug. 11, 1976, Pat. No. 4,021,488.

[51] Int. Cl.² **C07C 45/00**
[52] U.S. Cl. **260/586 C**
[58] Field of Search **260/586 C**

[56] **References Cited**

U.S. PATENT DOCUMENTS

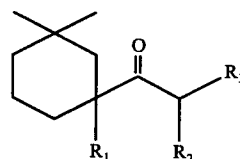
3,668,255	6/1972	Meuly et al.	260/586 C
3,701,814	10/1972	Mulhing	260/586 C
3,983,175	9/1976	Tamai et al.	260/586 C
4,018,718	4/1977	Ochsner et al.	260/586 C
4,045,489	8/1977	Wiegus et al.	260/586 C

Primary Examiner—Norman Morgenstern

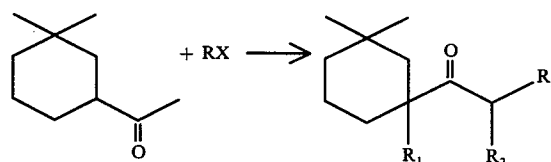
Attorney, Agent, or Firm—Arthur L. Liberman; Harold Haidt; Franklin D. Wolffe

[57] **ABSTRACT**

Described is a process for preparing a genus of substituted 1-acetyl-3,3-dimethylcyclohexanes having the structure:



wherein R₁ or one or both of R₂ and/or R₃ is allyl or methallyl and the other of R₁ or R₂ and/or R₃ is hydrogen, a process for preparing same by means of reacting an allyl or a methallyl halide with acetyl-3,3-dimethylcyclohexane using a base according to the reaction:



wherein R is allyl or methallyl and wherein X is chloro or bromo. When such 1-acetyl-3,3-dimethylcyclohexane derivatives are added to consumable materials:

- (i) In foodstuffs and medicinal products, pineapple, allyl caproate-like, galbanum, woody, fatty, sweet, fruity, citrus, green and vegetable-like aromas and rosey, ionone, Oriental-like, woody, fatty, sweet, fruity, citrus, vegetable-like and waxy flavor characteristics are augmented or enhanced;
- (ii) In perfumes and perfumed articles, sweet, earthy, animal, green, herbaceous, melony and fruity aromas with pineapple, ambery, galbanum-like, ginger-like and citrusy nuances and tobacco/animal notes are imparted, augmented and/or enhanced; and
- (iii) In tobaccos and tobacco flavors, green, sweet, fruity, floral and Virginia tobacco-like flavor and aroma nuances are augmented and/or enhanced in the main stream and in the side stream on smoking and, in addition, prior to smoking.

6 Claims, 7 Drawing Figures

FIG. 1

N M R SPECTRUM FOR EXAMPLES I, II, III, IV & V

SOLVENT: CDCl_3

SWEEP WIDTH: 1000 cps.

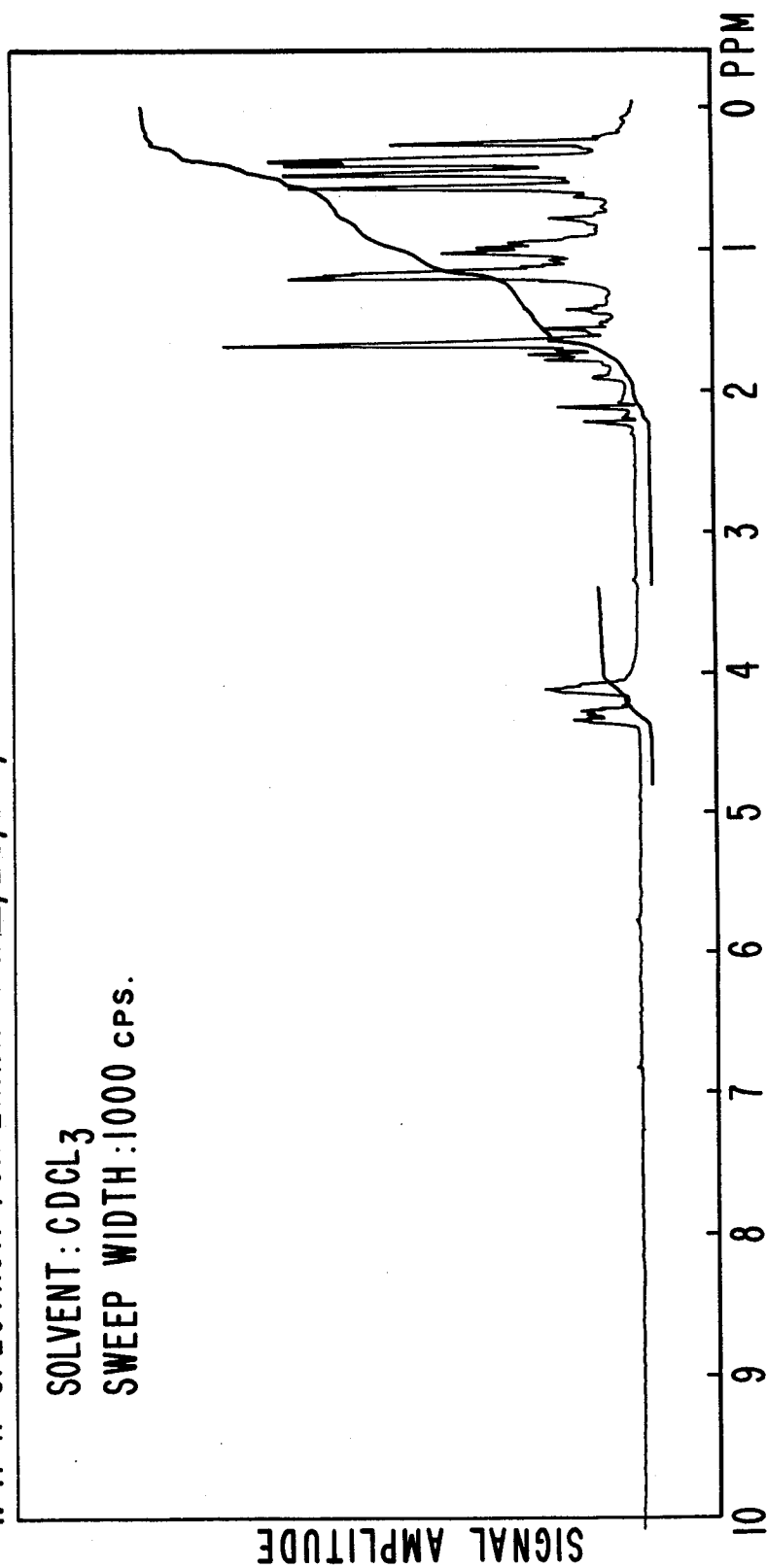
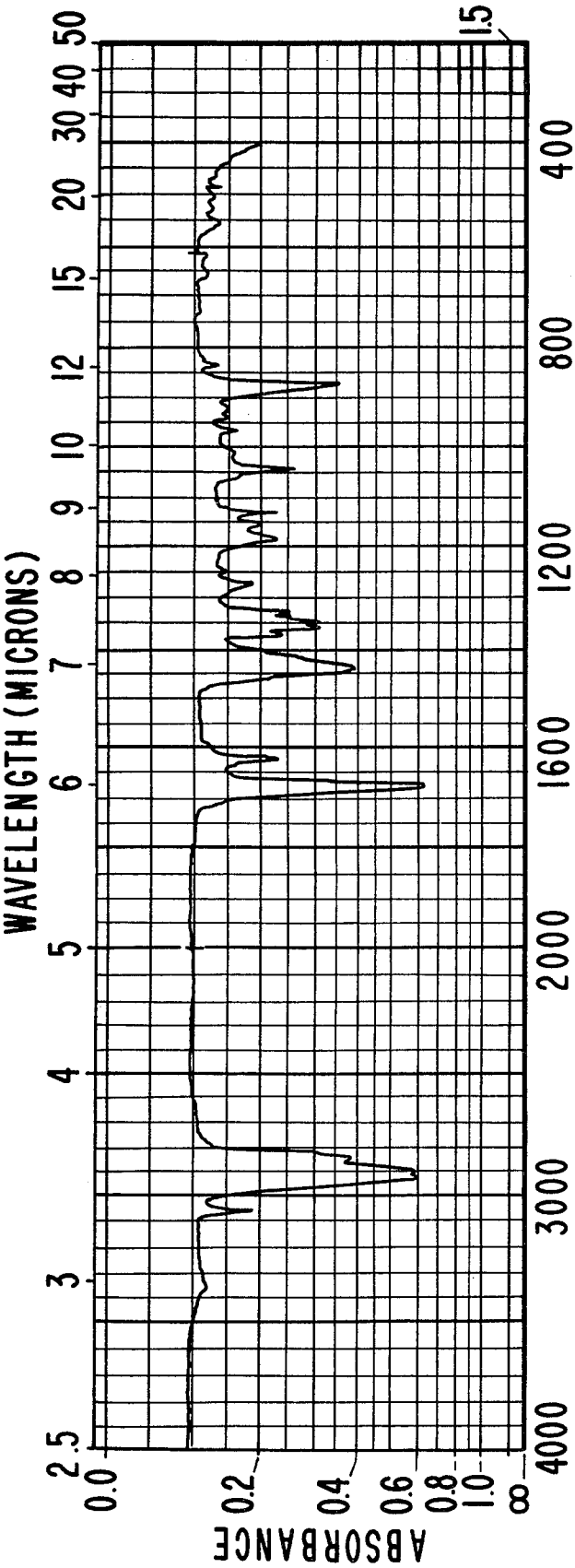


FIG. 2



I R SPECTRUM FOR EXAMPLES I, II, III, IV & V

FIG. 3

NMR SPECTRUM FOR EXAMPLE I

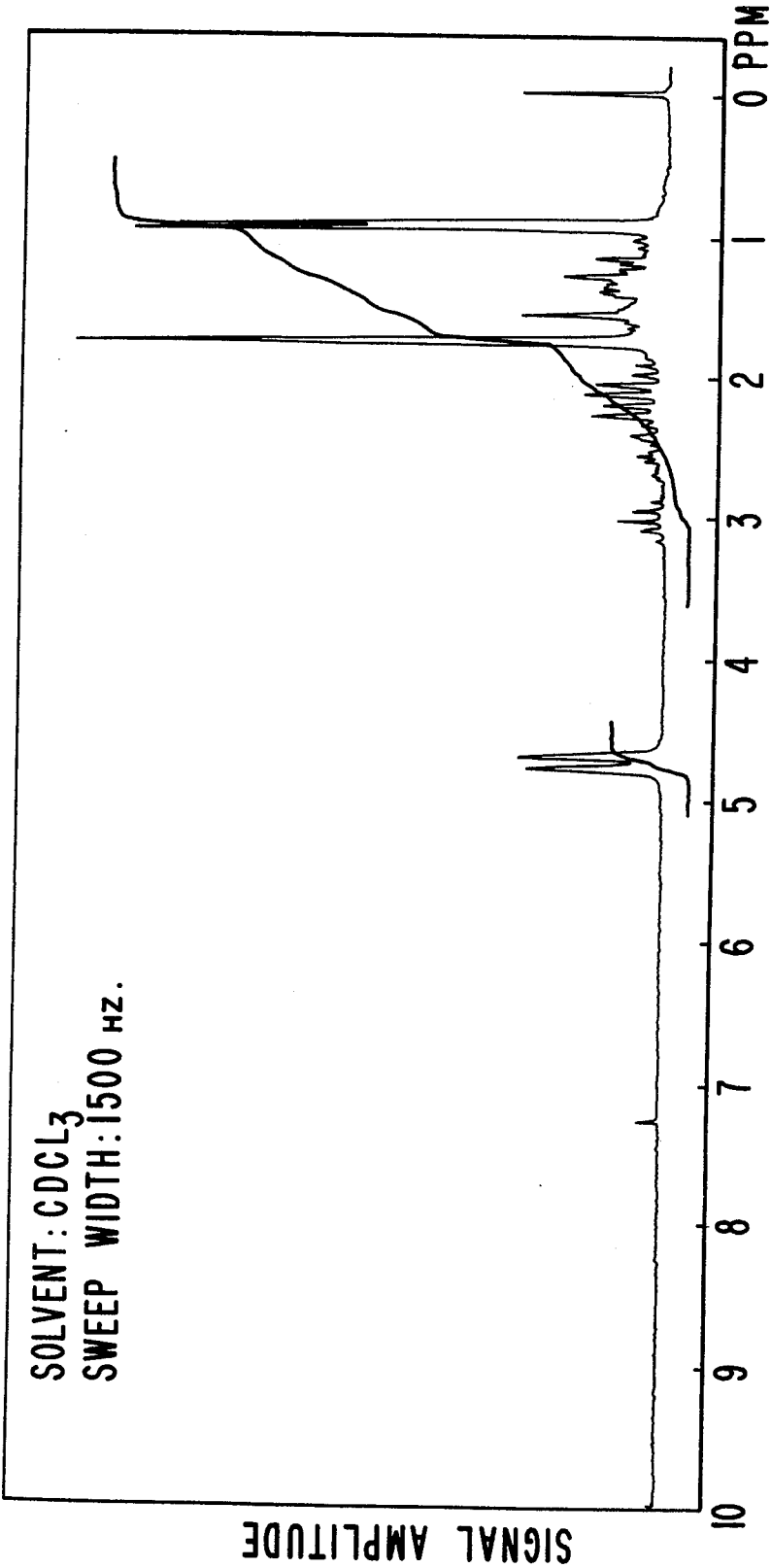
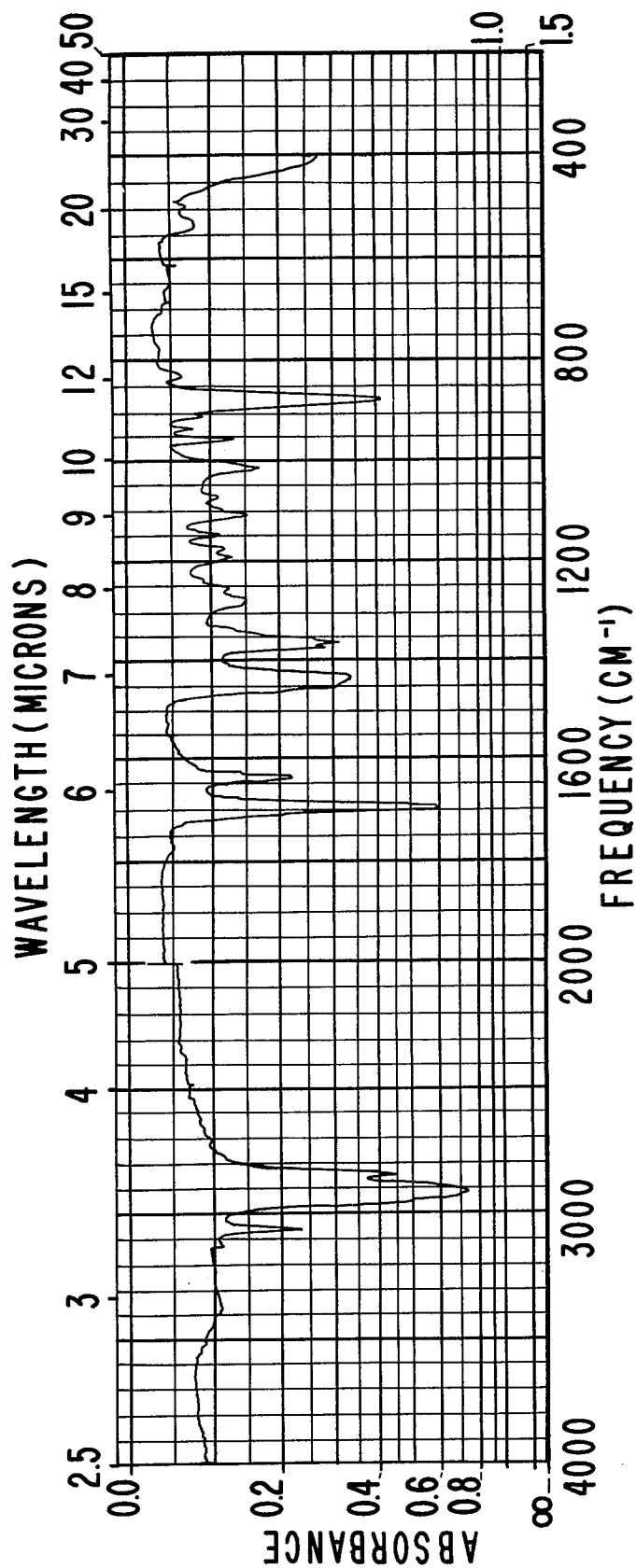


FIG. 4

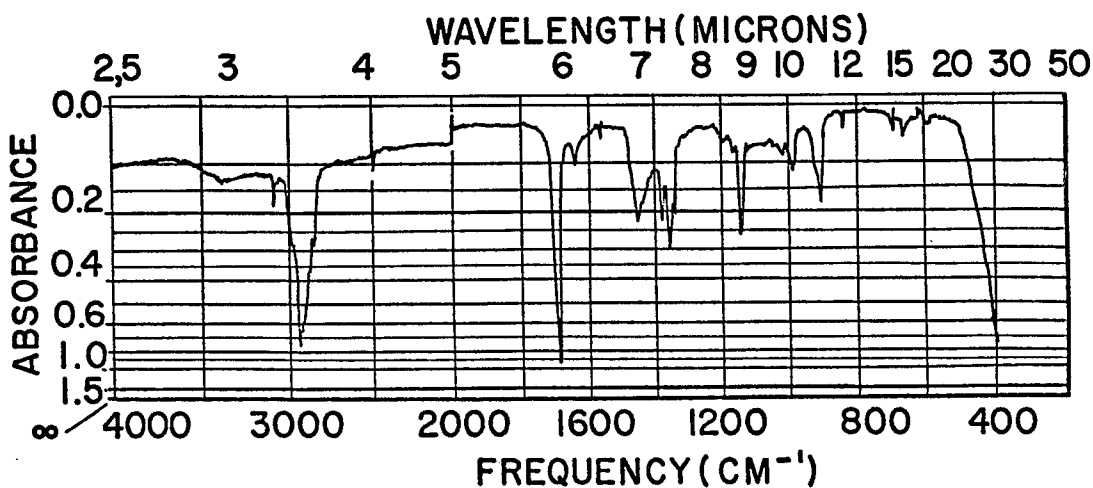
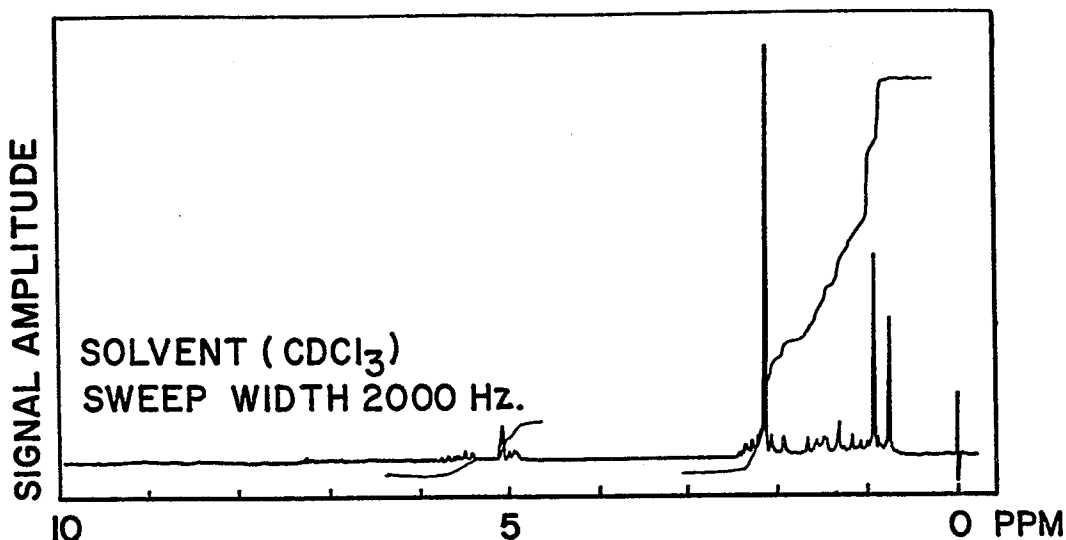


I R SPECTRUM FOR EXAMPLE I

FIG. 5EXAMPLES VI, VII, VIII AND IX

NMR SPECTRUM FOR

(1,1-DIMETHYL-3-ACETYL-3(2-PROPENYL)CYCLOHEXANE

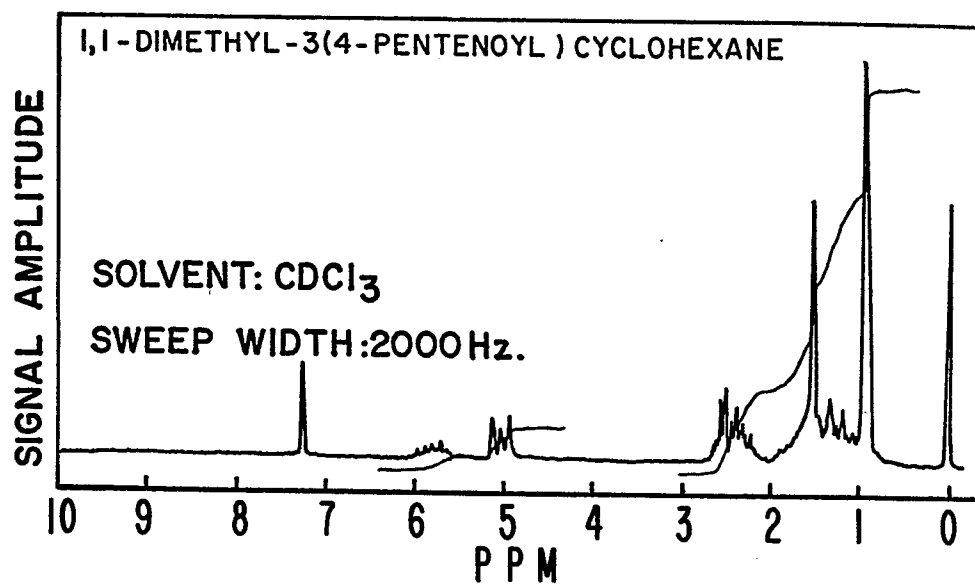


IR SPECTRUM FOR

(1,1-DIMETHYL-3-ACETYL-3(2-PROPENYL)CYCLOHEXANE

FIG. 6EXAMPLES VI, VII, VIII AND IX

FIG. 7

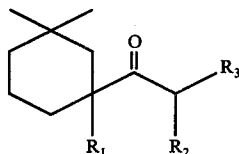
N M R SPECTRUM FOR EXAMPLES VI, VII AND VIII

PROCESS FOR PRODUCING SUBSTITUTED-1-ACETYL-3,3-DIMETHYLCYCLOHEXANE

This application is a continuation-in-part of application for U.S. Letters Patent Ser. No. 713,429, filed on Aug. 11, 1976, now U.S. Pat. No. 4,021,488.

BACKGROUND OF THE INVENTION

The present invention provides a process for producing 1-acetyl-3,3-dimethylcyclohexane derivatives having the generic structure:

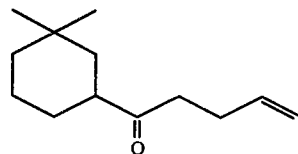


wherein R_1 or both of R_2 and/or R_3 is allyl or methallyl and the other of R_1 or R_2 and/or R_3 is hydrogen by reaction of an allyl or methallyl halide with acetyl-3,3-dimethylcyclohexane. The 1-acetyl-3,3-dimethylcyclohexane derivatives are useful for their organoleptic properties in perfumes, perfumed articles, foodstuffs, chewing gums, medicinal products, tobaccos and tobacco articles.

In the perfumery art there is a considerable need for substituents having sweet, earthy, animal, green, herbaceous, melony and fruity aromas with pineapple, ambery, galbanum-like, ginger-like and citrusy nuances and tobacco/animal notes. Specifically described are materials having such a profile but which do not discolor with age. Such fragrance materials have a wide utilization in perfume formulations and perfumed articles. A minimum amount of such materials that give rise to these properties is available from natural sources, but the natural materials are subject to wide variations in quality, are expensive and are limited or often in critically short supply.

Furthermore, there is a continuing search for compositions which can vary, modify, fortify, enhance, augment or otherwise improve the flavor and aroma of foodstuffs, chewing gums and medicinal products. To be satisfactory, such compositions should be stable, non-toxic and blendable with other ingredients to provide its own unique flavor and aroma nuance without detracting from the co-ingredients. Preferably, such compositions should be naturally occurring or present in natural foodstuffs so that their ingestible safety can be readily recognized or similar to those materials present in natural foodstuffs so that their ingestible safety can be recognized. These materials should be capable of being synthesized in a simple and economical manner. The need for safe flavors in the fruity flavor area, e.g. citrus flavor area, is well-known, particularly in the beverage flavor area and in the yogurt flavor area. More specifically, there is a need for the development of non-toxic materials which can replace natural materials not readily available, having pineapple, allyl caproate-like, galbanum, woody, fatty, sweet, fruity, citrus, green and vegetable aroma characteristics and rose, ionone-like, oriental-like, woody, sweet, fruity, and citrus flavor characteristics.

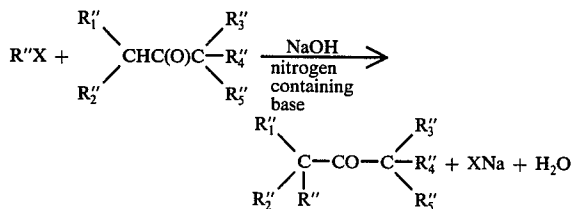
Firmenich's Dutch published application 7500838 discloses the preparation of the compound having the structure:



and discloses its use in perfumery and in augmenting foodstuff flavors. The perfumery use of this compound and other members of its class as "floral, green, herbaceous and chypre" useful in galbanum resinoids is also disclosed.

The compounds disclosed in Dutch published application 7500838 have organoleptic properties which cause them to be different in kind from the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention, which have unobvious, unexpected and advantageous characteristics in the field of augmenting or enhancing the organoleptic impressions of foodstuffs, foodstuff flavors, chewing gums, perfumes, perfumed articles, medicinal products, tobacco and tobacco flavors.

Insofar as relevant prior art concerning the process for preparing 1-acetyl-3,3-dimethylcyclohexane derivatives is concerned, German Pat. No. 1,244,784 issued on July 20, 1967, discloses the reaction:



wherein R'' can be one of alkyl, alkenyl, allyl, propargyl, cyclohexyl or benzyl; X is chloro or bromo and R''_1 , R''_2 , R''_3 , R''_4 and R''_5 can be hydrogen, alkyl, alkenyl or phenyl. The reaction of the German Patent is limited to ketones. However, the nature of the reaction is different in kind from the reaction of the instant invention.

German Pat. No. 1,244,784 corresponds to British Pat. No. 1,059,839 published on Feb. 22, 1967, entitled, "Process for Preparing Ketones and Novel Ketones so Prepared." Tamai, et al, U.S. Pat. No. 3,983,175 issued on Sept. 28, 1976, (a continuation-in-part of Ser. No. 417,201 filed on Nov. 19, 1973, now abandoned) discloses a process for producing substituted ketones by reacting an organic halide with a ketone which has a replaceable hydrogen atom on the carbon atom in the alpha position to the carbonyl group in the presence of an aqueous alkali metal hydroxide and a nitrogen-containing base as a catalyst, e.g., primary amines, secondary amines, tertiary amines, and quaternary ammonium salts. The nature of the reaction described in the patent by Tamai, et al, is different in kind from the reaction of the instant invention. The same holds true for Meuly, et al, U.S. Pat. 3,668,255 issued on June 6, 1972, a continuation-in-part of Ser. No. 241,036, filed Nov. 29, 1962, now abandoned.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 represents the NMR spectrum for 1-acetyl-1-methyl-3,3-dimethylcyclohexane produced according to Examples I, II, III, IV and V.

FIG. 2 represents the Infrared spectrum for 1-acetyl-1-methyl-3,3-dimethylcyclohexane produced according to Examples I, II, III, IV and V.

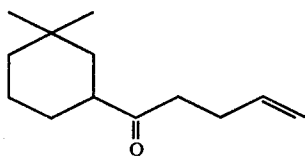
FIG. 3 represents the NMR spectrum for the compound 1-(2-methyl-5-methyl-4-pentenyl)-3,3-dimethylcyclohexane produced according to Example I.

FIG. 4 represents the Infrared spectrum for the compound 1-(2-methyl-5-methyl-4-pentenyl)-3,3-dimethylcyclohexane produced according to Example I.

FIG. 5 represents the NMR spectrum for 1-acetyl-3,3-dimethyl-(2-propenyl)cyclohexane produced according to Examples VI, VII, VIII and IX.

FIG. 6 represents the Infrared spectrum for 1-acetyl-3,3-dimethyl-(2-propenyl)cyclohexane produced according to Examples VI, VII, VIII and IX.

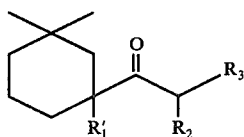
FIG. 7 represents the NMR spectrum for the compound having the structure:



produced according to Examples VI, VII and VIII.

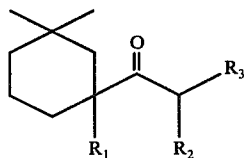
THE INVENTION

The present invention relates to processes for preparing the compounds, 1-acetyl-1(methyl or allyl)-3,3-dimethylcyclohexane and 1-(2(methyl or allyl)-5-methyl-4-pentenyl)-3,3-dimethylcyclohexane having the generic structure:



wherein one of R_1 or one or both of R_2 and/or R_3 is allyl or methylallyl and the other of R_1 or R_2 and/or R_3 is hydrogen, a process for producing same and perfumes, perfumed articles, foodstuffs, foodstuff flavorings, medicinal products, tobaccos and tobacco flavorings containing 1-acetyl-3,3-dimethylcyclohexane derivatives having the above generic structure.

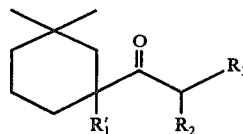
The compounds having the structure:



are capable of augmenting or enhancing orange flavors by providing thereto pineapple, allyl caproate-like, galbanum, woody, fatty, sweet, fruity, citrus, green aromas with rose, y, ionone, oriental-like, woody, sweet, fruity,

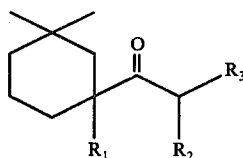
citrus flavor characteristics in conjunction with foodstuffs, chewing gums and medicinal products.

The compounds having the generic structure:

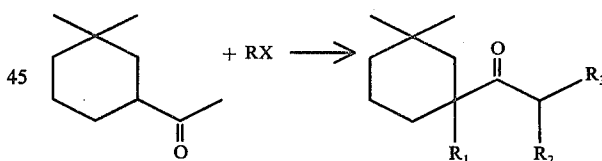


are also capable of modifying or enhancing the aroma characteristics of perfumed compositions and perfumed articles by imparting thereto or augmenting or enhancing sweet, earthy, animal, green, herbaceous, melony and fruity aromas with pineapple, ambery, galbanum-like, ginger and citrus nuances and tobacco/animal notes thus fulfilling a need in the field of perfumery.

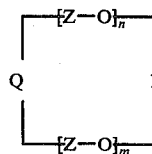
The compounds having the generic structure:



wherein one of R_1 or one or both of R_2 and/or R_3 is methylallyl or allyl, and the other of R_1 or R_2 and/or R_3 is hydrogen, are produced by reacting acetyl-3,3-dimethylcyclohexane with a methylallyl halide or an allyl halide in the presence of base such as an alkali metal hydroxide or potassium-t-butoxide and, further, in the presence of a third compound which may be either a tertiary amine, toluene, t-butanol or a crown ether (or various mixtures of same) (hereinafter referred to as a "reaction promoter") according to the following general reaction:

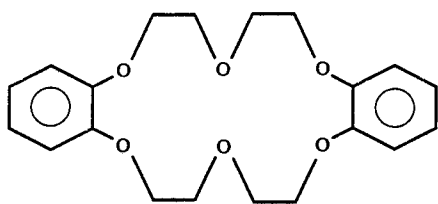


wherein R is allyl or methylallyl and X is chloro or bromo. The nature of the reaction product is primarily dependent upon the particular reaction promoter used, insofar as the isomer ratios of the reaction products are concerned. Thus, when crown ethers having the generic structure:



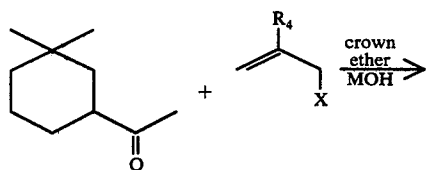
wherein Z is C_1 - C_4 lower alkylene, e.g., methylene or ethylene, N is from 3 up to 8, P and Q are the same or different and represent C_1 - C_4 lower alkylene or ortho phenylene, such as compounds having the structure:

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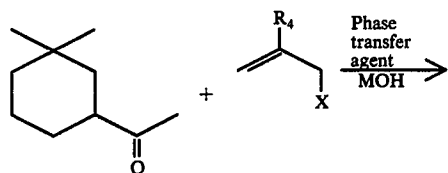


(dibenzo-18-crown 6) are used as reaction promoters, 15

the reaction product consists essentially of those prod-
ucts where the methallyl or allyl substituent is at the "1" 20
position on the ring, thus:

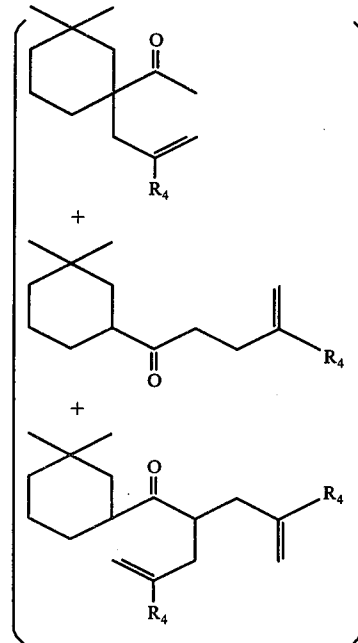


wherein R_4 is methyl or hydrogen and M is an alkali 45
metal. However, if a phase transfer agent is used as a
reaction promoter as exemplified in Example I, infra, 50
and as covered in U.S. Application for Letters Patent
Ser. No. 713,429 filed on Aug. 11, 1976, several by- 55
products are created, thus:



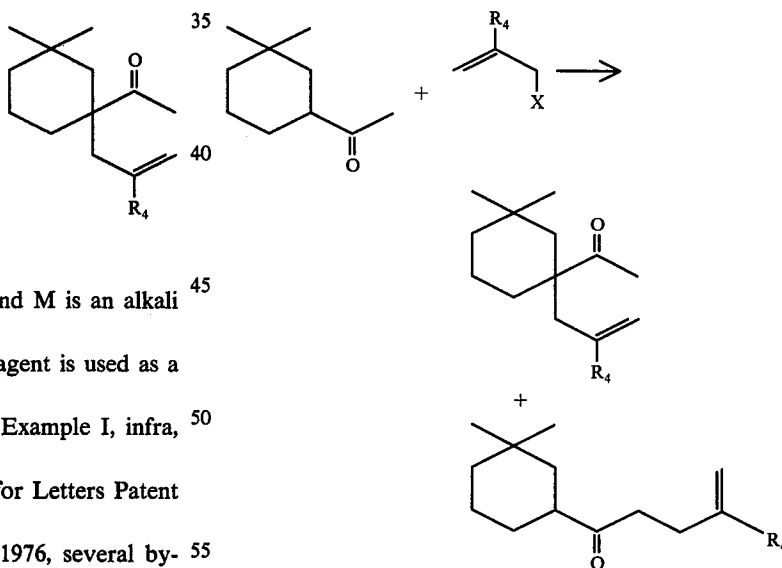
6

-continued



wherein R_4 is methyl or hydrogen, and X is chloro or bromo.

When a tertiary amine is used as a reaction promoter, or when toluene or t-butanol is used as a reaction promoter, the reaction that takes place is as follows:



wherein R_4 is methyl or hydrogen and X is chloro or bromo. Examples of tertiary amines which can be used in our invention are trimethyl amines, triethyl amines, dimethylaminoethyl dimethyl amine.

The process of our invention is carried out in an inexpensive solvent which is (a) inert to the reaction system and (b) may also serve as a reaction promoter. Among such solvents are toluene, benzene, o-xylene, m-xylene, p-xylene, ethyl benzene, n-hexane, cyclohexane, methylene chloride-dichlorobenzene, t-butanol and crown ethers such as dibenzo-18-crown-6.

The process of our invention is carried out at a temperature in the range of from about 10° C up to about 150° C with a temperature range of 50°–120° C being preferred. The reaction time is inversely proportional to the reaction temperature, with lower reaction temperatures giving rise to greater reaction times; and, accordingly, the reaction time ranges from about 30 minutes up to about 10 hours.

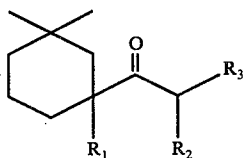
In each of the reactions of our invention, notwithstanding which reaction promoter is used, the mole ratio of 1-acetyl-3,3-dimethylcyclohexane to allyl halide or methallyl halide reactant is in the range of from 0.5:1.5 up to about 1.5:0.5 with a preferred ratio being from about 1:1 up to about 1:1.2.

The mole ratio of base:allyl halide or base:methallyl halide reactant in the reaction mass may be in the range of from about 0.75:1 up to about 1.5:1 with a preferred ratio of base:methallyl halide or base:allyl halide being from about 1:1 up to about 1.2:1.

The reaction of our invention is preferably carried out at atmospheric pressure since that is the most convenient condition, however, lower or higher pressures can be used without detrimentally affecting the ultimate yield of desired reaction product.

The particular base used in the reaction is critical and, preferred are, sodium hydroxide, potassium hydroxide and potassium-t-butoxide.

When the compounds having the generic structure:



wherein one of R_1 or one or both of R_2 and/or R_3 is methallyl or allyl and the other of R_1 or R_2 and/or R_3 is hydrogen (hereinafter referred to as "the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention") are used as food flavor adjuvants, the nature of the co-ingredients, included with the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention in formulating the product composition will also serve to alter, modify, augment or enhance the organoleptic characteristics of the ultimate foodstuff treated therewith.

As used herein in regard to flavors, the terms "alter", "modify" and "augment" in their various forms mean "supplying or imparting flavor character or note to otherwise bland, relatively tasteless substances or augmenting the existing flavor characteristic where a natural flavor is deficient in some regard or supplementing the existing flavor impression to modify its quality, character or taste".

The term "enhance" is used herein to mean the intensification of a flavor or aroma characteristic or note without the modification of the quality thereof. Thus, "enhancement" of a flavor or aroma means that the enhancement agent does not add any additional flavor note.

As used herein, the term "foodstuff" includes both solid and liquid ingestible materials which usually do, but need not, have nutritional value. Thus, foodstuffs include soups, convenience foods, beverages, dairy products, candies, chewing gums, vegetables, cereals, soft drinks, snacks and the like.

As used herein, the term "medicinal product" includes both solids and liquids which are ingestible non-toxic materials which have medicinal value such as

cough syrups, cough drops, aspirin and chewable medicinal tablets.

The term "chewing gum" is intended to mean a composition which comprises a substantially water-insoluble, chewable plastic gum base such as chicle, or substitutes therefor, including jelutong, guttakay, rubber or certain comestible natural or synthetic resins or waxes. Incorporated with the gum base in admixture therewith may be plasticizers or softening agents, e.g., glycerine; and a flavoring composition which incorporates the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention, and in addition, sweetening agents which may be sugars, including sucrose or dextrose and/or artificial sweeteners such as cyclamates or saccharin. Other optional ingredients may also be present.

Substances suitable for use herein as co-ingredients or flavoring adjuvants are well known in the art for such use, being extensively described in the relevant literature. It is a requirement that any such material be "ingestible" acceptable and thus non-toxic and otherwise non-deleterious particularly from an organoleptic standpoint whereby the ultimate flavor and/or aroma of the consumable material used is not caused to have unacceptable aroma and taste nuances. Such materials may in general be characterized as flavoring adjuvants or vehicles comprising broadly stabilizers, thickeners, surface active agents, conditioners, other flavorants and flavor intensifiers.

Stabilizer compounds include preservatives, e.g., sodium chloride; antioxidants, e.g., calcium and sodium ascorbate, ascorbic acid, butylated hydroxy-anisole (mixture of 2- and 3-tertiary-butyl-4-hydroxy-anisole), butylated hydroxy toluene (2,6-di-tertiary-butyl-4-methyl phenol), propyl gallate and the like and sequestrants, e.g., citric acid.

Thickener compounds include carriers, binders, protective colloids, suspending agents, emulsifiers and the like, e.g., agar agar, carrageenan; cellulose and cellulose derivatives such as carboxymethyl cellulose and methyl cellulose; natural and synthetic gums such as gum arabic, gum tragacanth; gelatin, proteinaceous materials; lipids; carbohydrates; starches, pectines, and emulsifiers, e.g., mono- and diglycerides of fatty acids, skim milk powder, hexoses, pentoses, disaccharides, e.g., sucrose corn syrup and the like.

Surface active agents include emulsifying agents, e.g., fatty acids such as capric acid, caprylic acid, palmitic acid, myristic acid and the like, mono- and diglycerides of fatty acids, lecithin, defoaming and flavor-dispersing agents such as sorbitan monostearate, potassium stearate, hydrogenated tallow alcohol and the like.

Conditioners include compounds such as bleaching and maturing agents, e.g., benzoyl peroxide, calcium peroxide, hydrogen peroxide and the like; starch modifiers such as peracetic acid, sodium chlorite, sodium hypochlorite, propylene oxide, succinic anhydride and the like, buffers and neutralizing agents, e.g., sodium acetate, ammonium bicarbonate, ammonium phosphate, citric acid, lactic acid, vinegar and the like; colorants, e.g., carminic acid, cochineal, tumeric and curcuma and the like; firming agents such as aluminum sodium sulfate, calcium chloride and calcium gluconate; texturizers, anti-caking agents, e.g., aluminum calcium sulfate and tribasic calcium phosphate; enzymes; yeast foods, e.g., calcium lactate and calcium sulfite; nutrient supplements, e.g., iron salts such as ferric phosphate, fer-

rous gluconate and the like, riboflavin, vitamins, zinc sources such as zinc chloride, zinc sulfate and the like.

Other flavorants and flavor intensifiers include organic acids, e.g., acetic acid, formic acid, 2-hexenoic acid, benzoic acid, n-butyric acid, caproic acid, caprylic acid, cinnamic acid, isobutyric acid, isovaleric acid, alpha-methyl-butyric acid, propionic acid, valeric acid, 2-methyl-2-pentenoic acid, and 2-methyl-3-pentenoic acid; ketones and aldehydes and ketals and acetals thereof, e.g., acetaldehyde, acetophenone, acetone, acetyl methyl carbinol, acrolein, n-butanal, crotonal, diacetyl, 2-methyl butanal, beta, beta-dimethylacrolein, methyl-n-amyl ketone, n-hexenal, 2-hexenal, isopentanal, hydrocinnamic aldehyde, cis-3-hexenal, 2-heptanal, nonyl aldehyde, 4-(p-hydroxyphenyl)-2-butanone, alpha-ionone, beta-ionone, methyl-3-butanone, benzaldehyde, damascone, damascenone, acetophenone, 2-heptanone, o-hydroxyacetophenone, 2-methyl-2-hepten-6-one, 2-octanone, 2-undecanone, 3-phenyl-4-pentenal, 2-phenyl-2-hexenal, 2-phenyl-2-pentenal, furfural, 5-methyl furfural, cinnamaldehyde, cis-ethylidene-cis-3-hexenal, cis-ethylidene-trans-3-hexenal, cis-ethylidene-trans-3-heptenal, cis-ethylidene-trans-3-heptenal-diethyl-acetal, cis-3-ethylidene-4-octenal, beta-cyclohomocitral, 2-pentanone, 2-pentenal an propanal; alcohols such as 1-butanol, benzyl alcohol, 1-borneol, trans-2-buten-1-ol, ethanol, geraniol, 1-hexanal, 2-heptanol, trans-2-hexenol-1, cis-3-hexen-1-ol, 3-methyl-3-buten-1-ol, 1-pentanol, 1-penten-3-ol, p-hydroxyphenyl-2-ethanol, isoamyl alcohol, isofenchyl alcohol, phenyl-2-ethanol, alpha-terpineol, cis-terpineol hydrate, eugenol, linalool, 2-heptanol, acetoin; esters, such as butyl acetate, ethyl acetate, ethyl acetoacetate, ethyl benzoate, ethyl butyrate, ethyl caprate, ethyl caproate, ethyl caprylate, ethyl cinnamate, ethyl crotonate, ethyl formate, ethyl isobutyrate, ethyl isovalerate, ethyl laurate, ethyl myristate, ethyl alpha-methylbutyrate, ethyl propionate, ethyl salicylate, trans-2-hexenyl acetate, hexyl acetate, 2-hexenyl butyrate, hexyl butyrate, isoamyl acetate, isopropyl butyrate, methyl acetate, methyl butyrate, methyl caproate, methyl isobutyrate, alpha-methyl-phenylglycidate, ethyl succinate, isobutyl cinnamate, cinnamyl formate, methyl cinnamate and terpenyl acetate; hydrocarbons such as dimethyl naphthalene, dodecane, methyl diphenyl, methyl naphthalene, myrcene, naphthalene, octadecane, tetradecane, tetramethyl naphthalene, tridecane, trimethyl naphthalene, undecane, caryophyllene, 1phellandrene, p-cymene, 1-alpha-pinene; pyrazines such as 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 3-ethyl-2,5-dimethylpyrazine, 2-ethyl-3,5,6-trimethylpyrazine, 3-isoamyl-2,5-dimethylpyrazine, 5-isoamyl-2,3-dimethylpyrazine, 2-isoamyl-3,5,6-trimethylpyrazine, isopropyl dimethylpyrazine, methyl ethylpyrazine, tetramethylpyrazine, trimethylpyrazine; essential oils, such as jasmine absolute, cassia oil, cinnamon bark oil, rose absolute, orris absolute, lemon essential oil, Bulgarian rose, yara yara and vanilla; lactones such as delta-nonalactone; sulfides, e.g., methyl sulfide and other materials such as maltol, acetoin and other acetals (e.g., 1,1-diethoxyethane, 1,1-dimethoxy-ethane and dimethoxy-methane).

The specific flavoring adjuvant selected for use may be either solid or liquid depending upon the desired physical form of the ultimate product, i.e., foodstuff, whether simulated or natural, and should, in any event, (i) be organoleptically compatible with the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention by not covering or spoiling the organoleptic properties

(aroma and/or taste) thereof; (ii) be non-reactive with the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention, and (iii) be capable of providing an environment in which the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention can be dispersed or admixed to provide a homogeneous medium. In addition, selection of one or more flavoring adjuvants, as well as the quantities thereof will depend upon the precise organoleptic character desired in the finished product. Thus, in the case of flavoring compositions, ingredient selection will vary in accordance with the foodstuff, chewing gum, medicinal product or toothpaste to which the flavor and/or aroma are to be imparted, modified, altered or enhanced. In contradistinction, in the preparation of solid products, e.g., simulated foodstuffs, ingredients capable of providing normally solid compositions should be selected such as various cellulose derivatives.

As will be appreciated by those skilled in the art, the amount of 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention employed in a particular instance can vary over a relatively wide range, depending upon the desired organoleptic effects to be achieved. Thus, correspondingly greater amounts would be necessary in those instances wherein the ultimate food composition to be flavored is relatively bland to the taste, whereas relatively minor quantities may suffice for purpose of enhancing the composition merely deficient in natural flavor or aroma. The primary requirement is that the amount selected be effective, i.e., sufficient to alter, modify or enhance the organoleptic characteristics of the parent composition, whether foodstuff per se, chewing gum per se, medicinal product per se, toothpaste per se, or flavoring composition.

The use of insufficient quantities of the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention will, of course, substantially vitiate any possibility of obtaining the desired results while excess quantities prove needlessly costly and in extreme cases, may disrupt the flavor-aroma balance, thus proving self-defeating. Accordingly, the terminology "effective amount" and "sufficient amount" is to be accorded a significance in the context of the present invention consistent with the obtention of desired flavoring effects.

Thus, and with respect to ultimate food compositions, chewing gum compositions, medicinal product compositions and toothpaste compositions, it is found that quantities of the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention ranging from a small but effective amount, e.g., 0.5 parts per million up to about 100 parts per million based on total composition are suitable. Concentrations in excess of the maximum quantity stated are not normally recommended, since they fail to prove commensurate enhancement of organoleptic properties. In those instances, wherein the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention are added to the foodstuff as an integral component of a flavoring composition, it is, of course, essential that the total quantity of flavoring composition employed be sufficient to yield an effective 1-acetyl-3,3-dimethylcyclohexane derivative concentration in the foodstuff product.

Food flavoring compositions prepared in accordance with the present invention preferably contain the 1-acetyl-3,3-dimethylcyclohexane derivative of our invention in concentrations ranging from about 0.1% up to about 15% by weight based on the total weight of the said flavoring composition.

The composition described herein can be prepared according to conventional techniques well known as typified by cake batters and fruit drinks and can be formulated by merely admixing the involved ingredients within the proportions stated in a suitable blender to obtain the desired consistency, homogeneity of dispersion, etc. Alternatively, flavoring compositions in the form of particulate solids can be conveniently prepared by mixing the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention with, for example, gum arabic, gum tragacanth, carrageenan and the like, and thereafter spray-drying the resultant mixture whereby to obtain the particular solid product. Pre-prepared flavor mixes in powder form, e.g., a fruit-flavored powder mix, are obtained by mixing the dried solid components, e.g., starch, sugar and the like and the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention in a dry blender until the requisite degree of uniformity is achieved.

It is presently preferred to combine with the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention, the following adjuvants:

p-Hydroxybenzyl acetone;
Geraniol;
Cassia Oil;
Acetaldehyde;
Maltol;
Ethyl methyl phenyl glycidate;
Benzyl acetate;
Dimethyl sulfide;
Eugenol;
Vanillin;
Caryophyllene;
Methyl cinnamate;
Guaiacol;
Ethyl pelargonate;
Cinnamaldehyde;
Methyl anthranilate;
5-Methyl furfural;
isoamyl acetate;
Cis-ethylidene-cis-3-hexenal;
Cis-ethylidene-trans-3-hexenal;
Cis-ethylidene-trans-3-heptenal;
Cis-ethylidene-trans-3-heptenal-diethylacetal;
Cis-3-ethylidene-4-octenal;
Isobutyl acetate;
Cuminaldehyde;
Alpha ionone;
Cinnamyl formate;
Ethyl butyrate;
Methyl cinnamate;
Acetic acid;
Gamma-undecalactone;
Naphthyl ethyl ether;
Diacetyl;
Furfural;
Ethyl acetate;
Anethole;
2,3-Dimethyl pyrazine;
2-Ethyl-3-methyl pyrazine;
3-Phenyl-4-pentenal;
2-Phenyl-2-hexenal;
2-Phenyl-2-pentenal;
3-Phenyl-4-pentenal diethyl acetal;
Damascone (1-crotonyl-2,2,6-trimethylcyclohex-1-one)
Damascenone (1-crotonyl-2,2,6-trimethylcyclohex-1,5-diene)

Beta-cyclohomocitral (2,2,6-trimethylcyclohex-1-ene carboxaldehyde)

Isoamyl butyrate;

Cis-3-hexenol-1;

2-Methyl-2-pentenoic acid;

Elemecine (4-allyl-1,2,6-trimethoxy benzene);

Isoelemecine (4-propenyl-1,2,6-trimethoxy benzene); and

2-(4-Hydroxy-4-methylpentyl) norbornadiene prepared according to U.S. Application for Letters Pat. No. 461,703, filed on Apr. 17, 1974

The 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention and one or more auxiliary perfume ingredients, including, for example, alcohols, aldehydes, ketones, terpinic hydrocarbons, nitriles, esters, lactones, natural essential oils and synthetic essential oils, may be admixed so that the combined odors of the individual components produce a pleasant and desired fragrance, particularly and preferably in petitgrain fragrances. Such perfume compositions usually contain (a) the main note or the "bouquet" or foundation stone of the composition; (b) modifiers which round off and accompany the main note; (c) fixatives which include odorous substances which lend a particular note to the perfume throughout all stages of evaporation and substances which retard evaporation; and (d) topnotes which are usually low boiling fresh smelling materials.

In perfume compositions, it is the individual components which contribute their particular olfactory characteristics, however, the over-all sensory effect of the perfume composition will be at least the sum total of the effects of each of the ingredients. Thus, the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention can be used to alter, modify or enhance the aroma characteristics of a perfume composition, for example, by utilizing or moderating the olfactory reaction contributed by another ingredient in the composition.

The amount of 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention which will be effective in perfume compositions as well as in perfumed articles and colognes depends on many factors, including the other ingredients, their amounts and the effects which are desired. It has been found that perfume compositions containing as little as 0.01% of 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention or even less (e.g., 0.005%) can be used to impart green, fruity, aldehydic notes with galbanum, ginger and citrus-like nuances to soaps, cosmetics or other products. The amount employed can range up to 70% of the fragrance components and will depend on considerations of cost, nature of the end product, the effect desired on the finished product and the particular fragrance sought.

The 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention are useful [taken alone or together with other ingredients in perfume compositions] as (an) olfactory component(s) in detergents and soaps, space odorants and deodorants; perfumes; colognes; toilet water; bath preparations such as bubble bath or bath salts; hair preparations such as lacquers, brilliantines, pomades and shampoos; cosmetic preparations, such as creams, deodorants, hand lotions and sun screens; powders, such as talcs, dusting powders, face powders and the like. When used as (an) olfactory component(s), as little as 1% of 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention will suffice to impart ginger, citrus and galbanum nuances to petitgrain aromas. Generally, no more than 3% of 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention, based on the

ultimate end product, is required in the perfume composition.

In addition, the perfume composition or fragrance composition of our invention can contain a vehicle, or carrier for the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention. The vehicle can be a liquid such as a non-toxic alcohol, a non-toxic glycol, or the like. The carrier can also be an absorbent solid, such as a gum (e.g., gum arabic) or components for encapsulating the composition (such as gelatin).

Furthermore, 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention are capable of supplying and/or potentiating certain flavor and aroma notes usually lacking in many tobacco flavors heretofore provided.

As used herein in regard to tobacco flavors, the terms "alter" and "modify" in their various forms mean "supplying or imparting flavor character or note to otherwise bland tobacco, tobacco substitutes, or tobacco flavor formulations or augmenting the existing flavor characteristic where a natural flavor is deficient in some regard or supplementing the existing flavor impression to modify its quality, character or taste".

As used herein, the term "enhance" is intended to mean the intensification (without change in kind or quality of aroma or taste) of one or more taste and/or aroma nuances present in the organoleptic impression of tobacco or a tobacco substitute or a tobacco flavor.

Our invention thus provides an organoleptically improved smoking tobacco product and additives therefor, as well as methods of making the same which overcome specific problems heretofore encountered in which specific desired green, sweet, fruity, floral and Virginia tobacco-like nuances prior to smoking and in the main and sidestreams on smoking, are created or enhanced and may be readily controlled and maintained at the desired uniform level regardless of variations in the tobacco components of the blend.

This invention further provides improved tobacco additives and methods whereby green, sweet, fruity, floral and Virginia tobacco-like nuances prior to smoking and in the main and sidestreams on smoking may be imparted to smoking tobacco products and may be readily varied and controlled to produce the desired uniform flavor characteristics.

In carrying out this aspect of our invention, we add to smoking tobacco materials or a suitable substitute therefor (e.g., dried lettuce leaves) an aroma and flavor additive containing as an active ingredient 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention.

In addition to the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention other flavoring and aroma additives may be added to the smoking tobacco materials or substitute therefor either separately or in mixture with the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention as follows:

I. Synthetic Materials:

Beta-ethyl-cinnamaldehyde;
Eugenol;
Dipentene;
Damascenone;
Maltol;
Ethyl Maltol;
Delta undecalactone;
Delta decalactone;
Benzaldehyde;
Amyl acetate;
Ethyl butyrate;
Ethyl valerate;

Ethyl acetate;
Beta-cyclohomocitral;
2-Hexenol-1,2-methyl-5-isopropyl-1,3-nonadiene-8-one;
2,6-Dimethyl-2,6-undecadiene-10-one;
2-Methyl-5-isopropyl acetophenone;
2-Hydroxy-2,5,5,8a-tetramethyl-1-(2-hydroxyethyl)-decahydronaphthalene;
Dodecahydro-3a,6,6,9a-tetramethyl naphtho-(2,1-b)-furan;
4-Hydroxy hexanoic acid, gamma lactone;
Polyisoprenoid hydrocarbons defined in Example V of U.S. Pat. No. 3,589,372 issued on June 29, 1971.

II. Natural Oils

Celery seed oil;
Coffee extract;
Bergamot Oil;
Cocoa extract;
Nutmeg oil;
Origanum oil

An aroma and flavoring concentrate containing 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention and, if desired, one or more of the above indicated additional flavoring additives may be added to the smoking tobacco material, to the filter or to the leaf or paper wrapper. The smoking tobacco material may be shredded, cured, cased and blended tobacco material or reconstituted tobacco material or tobacco substitutes (e.g., lettuce leaves) or mixtures thereof. The proportions of flavoring additives may be varied in accordance with taste but insofar as enhancement or the imparting of natural and/or sweet notes, we have found that satisfactory results are obtained if the proportion by weight of the sum total of 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention to smoking tobacco material is between 250 ppm and 1,500 ppm (0.025%-.15%) of the active ingredients to the smoking tobacco material. We have further found that satisfactory results are obtained if the proportion by weight of the sum total of 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention used to flavoring material is between 2,500 and 10,000 ppm (0.25%-1.5%).

Any convenient method for incorporating the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention in the tobacco product may be employed. Thus, the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention taken alone or along with other flavoring additives may be dissolved in a suitable solvent such as ethanol, pentane, diethyl ether and/or other volatile organic solvents and the resulting solution may either be spread on the cured, cased and blended tobacco material or the tobacco material may be dipped into such solution. Under certain circumstances, a solution of the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention taken alone or taken further together with other flavoring additives as set forth above, may be applied by means of a suitable applicator such as a brush or roller on the paper or leaf wrapper for the smoking product, or it may be applied to the filter by either spraying, or dipping, or coating.

Furthermore, it will be apparent that only a portion of the tobacco or substitute therefor need be treated and the thus treated tobacco may be blended with other tobaccos before the ultimate tobacco product is formed. In such cases, the tobacco treated may have the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention in excess of the amounts or concentrations above indicated so that when blended with other tobaccos, the

final product will have the percentage within the indicated range.

In accordance with one specific example of our invention, an aged, cured and shredded domestic burley tobacco is sprayed with a 20% ethyl alcohol solution of 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention in an amount to provide a tobacco composition containing 800 ppm by weight of 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention on a dry basis. Thereafter, the alcohol is removed by evaporation and the tobacco is manufactured into cigarettes by the usual techniques. The cigarette when treated as indicated has a desired and pleasing aroma (increased smoke body sensation in the mouth with enhanced tobacco-like notes and pleasant aromatic nuances) which is detectable in the main and sidestreams when the cigarette is smoked. This aroma is described as having green, sweet, fruity, floral and Virginia tobacco-like nuances prior to smoking and in the main and sidestreams on smoking.

While our invention is particularly useful in the manufacture of smoking tobacco, such as cigarette tobacco, cigar tobacco and pipe tobacco, other tobacco products formed from sheeted tobacco dust or fines may also be used. Likewise, the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention can be incorporated with materials such as filter tip materials, seam paste, packaging materials and the like which are used along with tobacco to form a product adapted for smoking. Furthermore, the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention can be added to certain tobacco substitutes of natural or synthetic origin (e.g., dried lettuce leaves) and, accordingly, by the term "tobacco" as used throughout this specification is meant any composition intended for human consumption by smoking or otherwise, whether composed of tobacco plant parts or substitute materials or both.

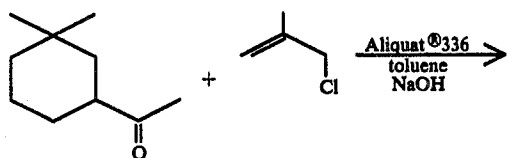
It will thus be apparent that the 1-acetyl-3,3-dimethylcyclohexane derivatives of our invention can be utilized to alter, modify or enhance sensory properties, such as flavor(s) and/or fragrance(s) of a wide variety of consumable materials.

The following Examples II—IX serve to illustrate our invention and the invention is to be considered restricted thereto only as indicated in the appended claims. Examples X—XXVI serve to illustrate the utilities of the products of the process of our invention.

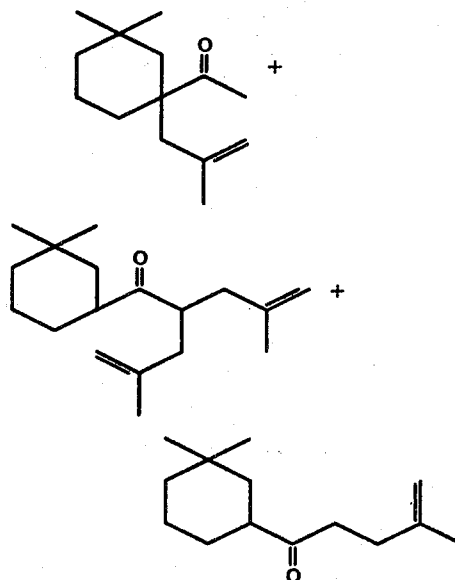
All parts and percentages given herein are by weight unless otherwise specified.

EXAMPLE I

PREPARATION OF 1-ACETYL-1-METHALLYL-3,3-DIMETHYLCYCLOHEXANE AND 1-(2-METHALLYL-5-METHYL-4-PENTENOYL)- 3,3-DIMETHYLCYCLOHEXANE Reaction:



-continued



A slurry of 1-acetyl-3,3-dimethylcyclohexane (624 grams, 4 moles), granular sodium hydroxide (240 grams, 6 moles), Aliquat® 336 (tricaprylmethylammonium chloride [35 grams]), methallyl chloride (432 grams, 4.8 moles), and 400 ml of toluene is heated at reflux for 4½ hours. At the end of this time, one liter of water is added to the cooled reaction mass. The aqueous layer is discarded, and the organic layer is distilled rapidly through a short column to afford 203 grams of recovered 1-acetyl-3,3-dimethylcyclohexane, 500 grams of 1-acetyl-3,3-dimethyl-1-methallylcyclohexane (104°, 3.0 mm Hg, containing 5% 3,3-dimethyl-(4-methyl-4-pentenyl)cyclohexane) and 73 grams of 3,3-dimethyl-1-(2-methallyl-5-methyl-4-pentenyl) cyclohexane. A portion of the latter compound is isolated by GLC chromatography (1' × ¼ inch 80% SE-30 packed column; 200° C isothermal) and exhibits the following odor and flavor properties.

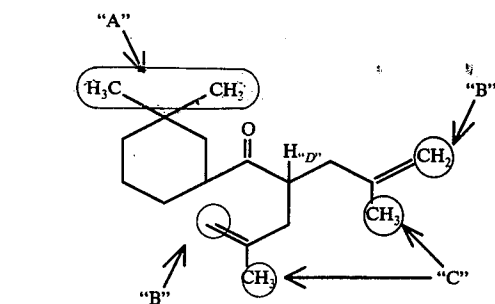
Odor Properties

Green;
Herbaceous;
Melony;
Fruity;
Galbanum-like;
Ginger-like; and
Citrusy.

Flavor Properties

Fatty;
Sweet;
Fruity;
Citrus;
Green;
Vegetable-like; and
Waxy.

The NMR analyses for the structures set forth below are as follows:



ppm	Interpretation
0.92 (s, 3)	methyl groups "A"
0.94 (s, 3)	
1.70 (s, 6)	methyl groups "C"
3.02 (quintet, 1, J=6H)	H _D
4.76 (d, 4, J=8H)	methyl groups "B"

The infrared analysis is as follows:

C=O	1695 cm ⁻¹
C=CH ₂	1635 cm ⁻¹

The Mass Spectral analysis is as follows:

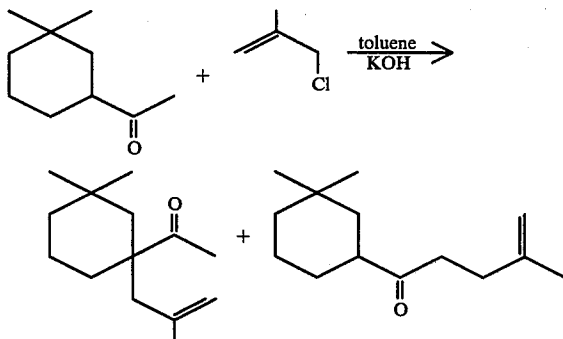
MW-262 (confirmed by GC-MS)

The NMR spectrum is set forth in FIG. 1 for 1-acetyl-3,3-dimethyl-1-methylallylcyclohexane. The Infrared spectrum is set forth in FIG. 2 for 1-acetyl-3,3-dimethyl-1-methylallylcyclohexane.

The NMR spectrum for 3,3-dimethyl-1-(2-methyl-5-methyl-4-pentenyl) cyclohexane is set forth in FIG. 3. The Infrared spectrum is set forth in FIG. 4.

EXAMPLE II

Reaction:



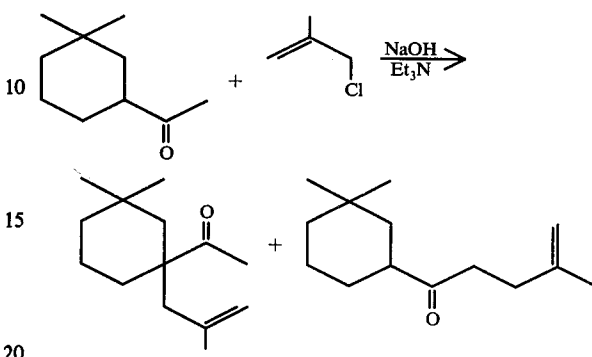
A slurry of 1-acetyl-3,3-dimethylcyclohexane (156 grams, 1 mole), potassium hydroxide (86 grams, 1.5 moles), and toluene (300 ml) is heated to reflux. Methallyl chloride (135 grams, 1.5 moles) is added to the thickened reaction mass whereupon the mass becomes more fluid. The mixture is heated at reflux for 6½ hours. At the end of this period, the reaction mass is cooled to room temperature, and 500 ml of water are added thereto. The aqueous layer is discarded, and the organic layer is distilled to afford recovered 1-acetyl-3,3-dimethylcyclohexane (86 gm), 1-acetyl-3,3-dimethyl-1-methylallylcyclohexane (67 gm, containing 2% 3,3-dimethyl-1-(4-methyl-4-pentenyl) cyclohexane) (NMR spectrum, FIG. 1; IR spectrum, FIG. 2) and

3,3-dimethyl-1-(4-methyl-4-pentenyl) cyclohexane (12 gm)

EXAMPLE III

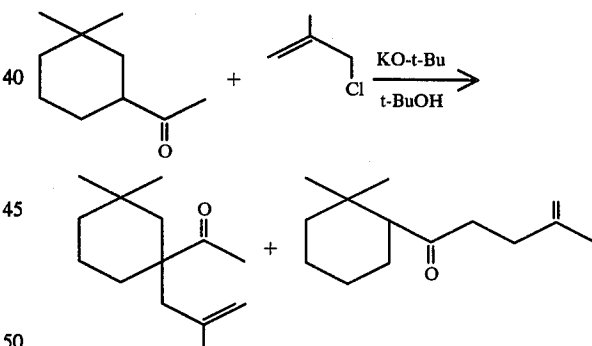
5

Reaction:



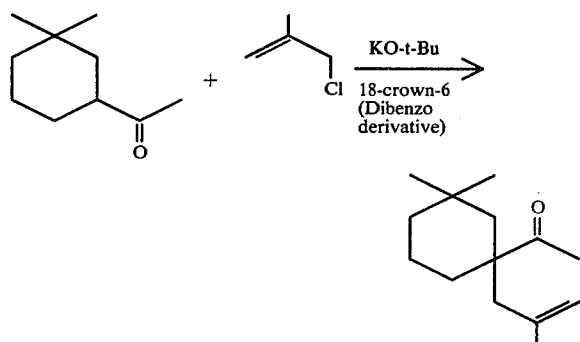
A mixture of 1-acetyl-3,3-dimethylcyclohexane (156 grams, 1 mole), sodium hydroxide (60 grams, 1.5 moles), methallyl chloride (135 grams, 1.5 moles) and triethylamine (10 grams) is stirred and heated at 80°-84° C for 12 hours. The reaction mass is cooled to room temperature. Water is added with stirring, and the aqueous layer is discarded. The organic layer is distilled to afford 1-acetyl-3,3-dimethylcyclohexane (62.4 gm), 1-acetyl-3,3-dimethyl-1-(2-methyl-2-propenyl) cyclohexane (80 gm) (NMR spectrum, FIG. 1; IR spectrum, FIG. 2) and 3,3-dimethyl-1-(4-methyl-4-pentenyl) cyclohexane (8 gm).

EXAMPLE IV

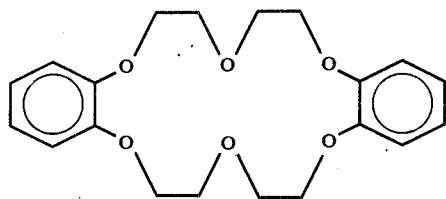


A fresh solution of potassium-t-butoxide is prepared by adding potassium metal (28 grams, 0.72 moles) to 500 ml of anhydrous t-butanol under a nitrogen blanket. 1-Acetyl-3,3-dimethylcyclohexane is added thereto, and the resulting mixture is stirred at room temperature for 1 hour. Methallyl chloride (74.4 gms, 0.8 moles) is added, and the reaction mass is allowed to stir for an additional hour. The mixture is filtered to remove potassium chloride, and the t-butanol is removed by evaporation on a rotary evaporator. The residual oil is distilled to afford a mixture of 1-acetyl-3,3-dimethyl-1-(2-methyl-2-propenyl) cyclohexane, 1-acetyl-3,3-dimethyl-1-(2-methyl-2-propenyl)cyclohexane, and 3,3-dimethyl-1-(4-methyl-4-pentenyl) cyclohexane (5:1y:1, GLC integration: GLC conditions, 10% SE-30 packed column, ¼ inch × 10', 200° isothermal).

EXAMPLE V

PREPARATION OF
1-ACETYL-3,3-DIMETHYL-(2-METHYL-2-PROPENYL) CYCLOHEXANE

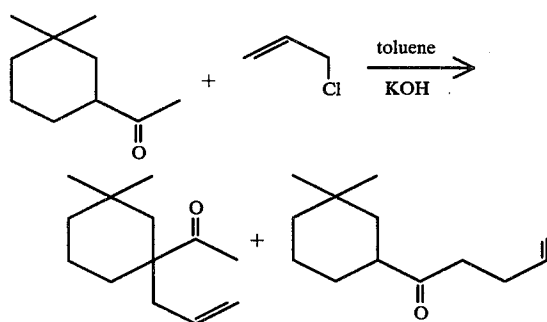
A slurry of potassium hydroxide (84 grams, 1.5 moles), 1-acetyl-3,3-dimethylcyclohexane (156 grams, 1 mole), dibenzo-18-crown-6 (3 grams) having the structure:



produced by the Aldrich Chemical Company of Metuchen, New Jersey, and toluene (150 ml) is heated to reflux whereupon the reaction mass thickens. The mass is cooled to 70° C, and methallyl chloride (135 grams, 1.5 moles) is added thereto rendering the reaction mixture more fluid. The reaction mixture is heated at reflux for an additional 9 hours whereupon the mass is cooled, and water is added. The aqueous layer is decanted, and the organic layer is distilled to afford 3,3-dimethylcyclohexane (62 gm) and 1-acetyl-3,3-dimethyl-1-(2-methyl-2-propenyl) cyclohexane (83 gm) (NMR spectrum, FIG. 1; IR spectrum, FIG. 2).

EXAMPLE VI

Reaction:



A slurry of 1-acetyl-3,3-dimethylcyclohexane (156 grams, 1 mole), potassium hydroxide (86 grams, 1.5 moles), and toluene (300 ml) is heated to reflux. Allyl chloride (114 grams, 1.5 moles) is added to the thick-

ened reaction mass whereupon the mass becomes more fluid. The mixture is heated at reflux for 6½ hours. At the end of this period, the reaction mass is cooled to room temperature, and 500 ml of water is added thereto. The aqueous layer is discarded, and the organic layer is distilled to afford 74 grams of recovered 1-acetyl-3,3-dimethyl hexane, 53 grams of 1-acetyl-3,3-dimethyl-1-(2-propenyl) cyclohexane, and 35 grams of 3,3-dimethyl-1-(4-pentenyl) cyclohexane.

The NMR spectrum for the 1-acetyl-3,3-dimethyl-1-(2-propenyl) cyclohexane is set forth in FIG. 5. The Infrared spectrum is set forth in FIG. 6.

The NMR analysis is as follows:

8. ppm	Interpretation
0.74 (s,3)	methyl groups "A"
0.09 (s,3)	CH ₃ Group "B"
2.14 (s,3)	Interpretation
8. ppm	Interpretation
4.8 → 5.1 (m, 2)	CH ₂ Group "C"
5.4 → 5.8 (m, 1)	H _D

The Infrared analysis is as follows:

C=O; 1690 cm⁻¹

C=C; 1660

The Mass Spectral analysis is as follows: m/e = 95, 94, 69, 41, 109, 55, 194 (parent peak). The NMR analysis for 3,3-dimethyl-1-(4-pentenyl) cyclohexane is set forth in FIG. 7 and is as follows:

8, ppm	Interpretation
0.90 (s,3)	Methyl Groups "A"
0.93 (s,3)	CH ₃ 's "B" and H _C
2.2 → 2.65 (m, 5)	CH ₂ "D"
4.60 → 5.12 (m, 2)	H _E
5.50 → 5.95 (m, 1)	

The Mass Spectral analysis is as follows:

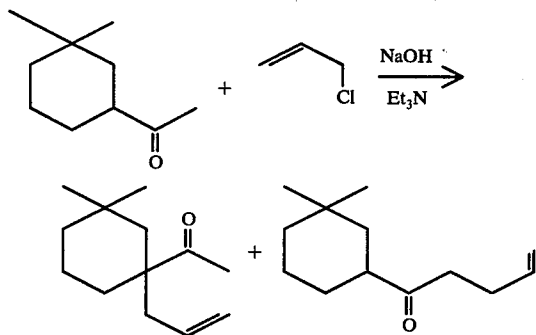
m/e = 69, 111, 55, 41, 83, 139, 194 (parent peak).

EXAMPLE VIII

Reaction

21

-continued

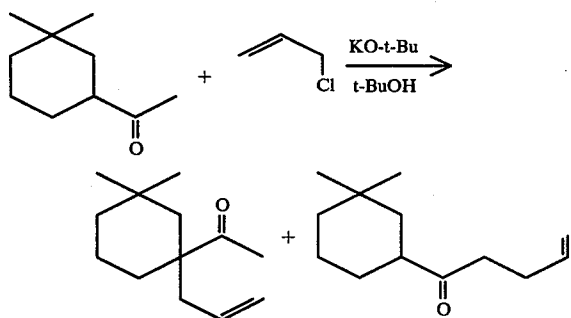


A mixture of 1-acetyl-3,3-dimethylcyclohexane (156 grams, 1 mole), sodium hydroxide (60 grams, 1.5 moles), allyl chloride (114 grams, 1.5 moles) and triethylamine (10 grams) is stirred and heated at 80°–84° C for 12 hours. The reaction mass is cooled to room temperature. Water is added with stirring, and the aqueous layer is discarded. The organic layer is distilled to afford 119 grams of 1-acetyl-3,3-dimethylcyclohexane, 31 grams of 1-acetyl-3,3-dimethyl-1-(2-propenyl) cyclohexane, and 5 grams of 3,3-dimethyl-1-(4-pentenyl) cyclohexane.

The NMR spectrum for 1-acetyl-3,3-dimethyl-1-(2-propenyl) cyclohexane is set forth in FIG. 5. The Infrared spectrum is set forth in FIG. 6. The NMR spectrum for 3,3-dimethyl-1-(4-pentenyl) cyclohexane is set forth in FIG. 7.

EXAMPLE VIII

Reaction:



A fresh solution of potassium-t-butoxide is prepared by adding potassium metal (28 grams, 0.72 moles) to 500 ml of anhydrous t-butanol under a nitrogen blanket. 1-Acetyl-3,3-dimethylcyclohexane is added thereto, and the resulting mixture is stirred at room temperature for 1 hour. Allyl chloride (63.2 grams, 0.8 moles) is added, and the reaction mass is allowed to stir for an additional hour. The mixture is filtered to remove potassium chloride, and the t-butanol is removed by evaporation on a rotary evaporator. The residual oil is distilled to afford 78 grams of a 13:1 mixture of 1-acetyl-3,3-dimethyl-1-(2-propenyl) cyclohexane and 3,3-dimethyl-1-(4-pentenyl) cyclohexane (ratio determined by integration of GLC chromatogram. GLC conditions: 10' × 1/4 inch 10% SE-30 packed column, 200° C isothermal), and 41 grams of nonvolatile material.

The NMR spectrum for 1-acetyl-3,3-dimethyl-1-(2-propenyl) cyclohexane is set forth in FIG. 5. The Infrared spectrum is set forth in FIG. 6. The NMR spectrum

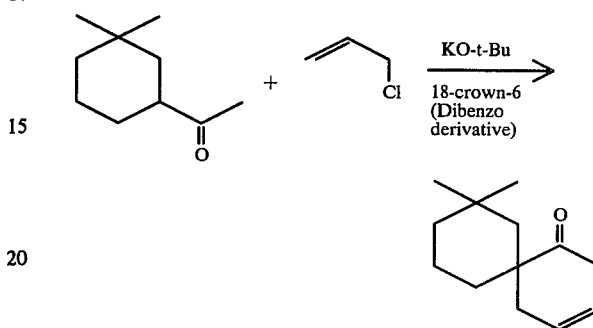
22

for 3,3-dimethyl-1-(4-pentenyl) cyclohexane is set forth in FIG. 7.

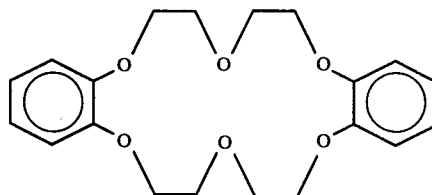
EXAMPLE IX

PREPARATION OF 1-ACETYL-3,3-DIMETHYL-(2-PROPENYL) CYCLOHEXANE

Reaction:



A slurry of potassium hydroxide (84 grams, 1.5 moles), 1-acetyl-3,3-dimethyl cyclohexane (156 grams, 1 mole), dibenzo-18-crown-6 (3 grams) having the structure:



produced by the Aldrich Chemical Company of Metuchen, New Jersey, and toluene (150 ml) is heated to reflux whereupon the reaction mass thickens. The mass is cooled to 70° C, and allyl chloride (114 grams, 1.5 moles) is added thereto rendering the reaction mixture more fluid. The reaction mixture is heated at reflux for an additional 9 hours whereupon the mass is cooled, and water is added. The aqueous layer is added, and the organic layer is distilled to afford 24 grams of 3,3-dimethylcyclohexane, 48 grams of 1-acetyl-3,3-dimethyl-1-(2-propenyl)cyclohexane, and 90 grams of nonvolatile material.

The NMR spectrum for 1-acetyl-3,3-dimethyl-1-(2-propenyl) cyclohexane is set forth in FIG. 5. The Infrared spectrum is set forth in FIG. 6.

EXAMPLE X

A tobacco blend is made up by mixing the following materials:

Ingredient	Parts by Weight
Bright	40.1
Burley	24.9
Maryland	1.1
Turkish	11.6
Stem (flue cured)	14.2
Glycerine	2.8
Water	5.3

The above tobacco is used in producing cigarettes and the following formulation is compounded and incorporated into each of these cigarettes.

Ingredient	Parts by Weight
Ethyl butyrate	.05
Ethyl valerate	.05
Maltol	2.00
Cocoa extract	26.00
Coffee extract	10.00
Ethyl alcohol	20.00
Water	41.90

The above flavor is incorporated into model "filter" cigarettes at the rate of 0.1%. One-third of these model cigarettes are treated in the tobacco section with 1-acetyl-1-methallyl-3,3-dimethylcyclohexane produced according to each of Examples II, III, IV and V at 100 ppm per cigarette. Another third of these model cigarettes are treated in the filter with 1-acetyl-1-methallyl-3,3-dimethylcyclohexane at the rate of 2×10^{-5} gm. and 3×10^{-5} gm. When evaluated by paired comparison, the cigarettes treated both in the tobacco and in the filter with 1-acetyl-1-methallyl-3,3-dimethylcyclohexane are found, in smoke flavor, to have a green, sweet, fruity, floral and Virginia tobacco-like flavor and aroma nuance in the mainstream and in the sidestream on smoking and, in addition, prior to smoking.

EXAMPLE XI

A tobacco blend is made up by mixing the following materials:

Ingredient	Parts by Weight
Bright	40.1
Burley	24.9
Maryland	1.1
Turkish	11.6
Stem (flue cured)	14.2
Glycerine	2.8
Water	5.3

The above tobacco is use in producing cigarettes and the following formulation is compounded and incorporated into each of these cigarettes.

Ingredient	Parts by Weight
Ethyl butyrate	.05
Ethyl valerate	.05
Maltol	2.00
Cocoa extract	26.00
Coffee extract	10.00
Ethyl alcohol	20.00
Water	41.90

The above flavor is incorporated into model "filter" cigarettes at the rate of 0.1%. One-third of these model cigarettes are treated in the tobacco section with the 1-acetyl-1-allyl-3,3-dimethylcyclohexane produced according to each of Examples VI, VII and VIII at 100 ppm per cigarette. Another third of these model cigarettes are treated in the filter with the 1-acetyl-1-allyl-3,3-dimethylcyclohexane at the rate of 2×10^{-5} gm. and 3×10^{-5} gm. When evaluated by paired comparison, the cigarettes treated both in the tobacco and in the filter with 1-acetyl-1-allyl-3,3-dimethylcyclohexane are found, in smoke flavor, to have a green, sweet, fruity, floral and Virginia tobacco-like flavor and aroma nuance in the mainstream and in the sidestream on smoking and, in addition, prior to smoking.

EXAMPLE XII

ORANGE FLAVOR FORMULATION

An orange flavor formulation is prepared by admixing:

Ingredients	Parts
Natural orange oil	13.00
Acetaldehyde	1.50
Ethyl acetate	0.10
Ethyl butyrate	0.50
Propanol	0.10
trans-2-Hexenal	0.10
Ethyl alcohol (95%)	60.00
Fusel Oil	0.05
Propylene Glycol	24.65

This is denominated Flavor "A". A second formulation, Flavor "B," is prepared by adding 1-acetyl-1-methallyl-3,3-dimethylcyclohexane prepared according to Example V (one percent in ethanol) to a portion of Flavor "A" in the ratio of 2 parts to 100 parts of Flavor "A".

Each of Flavors "A" and "B" is added in the amount of two ounces per gallon of 32° Baume sugar syrup to produce a syrup for combination with water to form a drink. The beverage prepared using Flavor "A" is a passable orange beverage of good character, flavor and intensity.

The beverage prepared using Flavor "B" has a much improved flavor. The improvement contributed by 1-acetyl-1-methallyl-3,3-dimethylcyclohexane prepared according to Example V is due to:

1. a greater degree of the natural character of freshly squeezed orange juice and
2. greater orange juice flavor depth.

EXAMPLE XIII

A perfume composition is prepared by admixing the following ingredients in the indicated proportions:

Ingredient	Amount (Grams)
n-Decyl Aldehyde	1
n-Dodecyl Aldehyde	2
Methyl Nonyl Acetaldehyde	0.5
Linalool	50
Linalyl Acetate	70
Phenyl Ethyl Alcohol	100
Petigrain SA	20
Bergamot Oil	30
Alpha Methyl Ionone	25
1-Acetyl-3,3-dimethyl-(2-propenyl)cyclohexane produced according to the process of Example VI	30
Cyclized Bicyclo C-12 material produced according to the process of Example IV of Canadian Patent 854,225, issued on October 20, 1970	5
Isobornyl cyclohexyl alcohol	10
Benzyl Acetate	25
2-n-Heptyl cyclopentanone	5
	353.3 (TOTAL)

The foregoing blend is evaluated and found to have a high degree of richness and persistence in its novel natural amber quality. This base composition can be admixed with aqueous ethanol, chilled and filtered to produce a finished cologne. The cologne so prepared has an amber aroma leaning towards a woody amber note. The base composition can also be used to scent soap or other toilet goods such as lotion, aerosol, sprays and the like.

EXAMPLE XIV

PREPARATION OF A COSMETIC POWDER
COMPOSITION

A cosmetic powder is prepared by mixing in a ball mill, 100 g of talcum powder with 0.25 g of 1-acetyl-3,3-dimethyl-(2-propenyl)cyclohexane produced according to Example VII. It has an excellent woody, earthy, amber aroma.

EXAMPLE XV

PERFUMED LIQUID DETERGENT

Concentrated liquid detergents with woody, earthy and amber aromas (which detergents are produced from Lysine salt of n-dodecyl benzene sulfonic acid as more specifically described in U.S. Pat. No. 3,948,818, issued on Apr. 6, 1976) are prepared containing 0.10%, 0.15% and 0.20% of 1-acetyl-3,3-dimethyl-(2-propenyl)cyclohexane prepared according to Example IX. They are prepared by adding and homogeneously mixing the appropriate quantity of 1-acetyl-3,3-dimethyl-(2-propenyl)cyclohexane in the liquid detergent. The detergents all possess a woody, earthy, amber aroma, the intensity increasing with greater concentrations of 1-acetyl-3,3-dimethyl-(2-propenyl)cyclohexane.

EXAMPLE XVI

PREPARATION OF A COLOGNE AND
HANDKERCHIEF PERFUME

1-Acetyl-3,3-dimethyl-(2-propenyl)cyclohexane, prepared according to the process of Example IX is incorporated in a cologne at a concentration of 2.5% in 85% aqueous ethanol; and into a handkerchief perfume at a concentration of 20% (in 95% aqueous ethanol). A distinct and definite woody, earthy, amber aroma is imparted to the cologne and to the handkerchief perfume.

EXAMPLE XVII

PREPARATION OF A COLOGNE AND
HANDKERCHIEF PERFUME

The composition of Example II is incorporated in a cologne at a concentration of 2.5% in 85% aqueous ethanol; and into a handkerchief perfume at a concentration of 20% (in 95% aqueous ethanol). The use of the 1-acetyl-3,3-dimethyl-(2-propenyl)cyclohexane in the composition of Example XIII affords a distinct and definite strong woody, earthy, amber aroma to the handkerchief perfume and cologne.

EXAMPLE XVIII

PREPARATION OF SOAP COMPOSITION

One hundred grams of soap chips are mixed with two grams of the composition of Example XIII until a substantially homogeneous composition is obtained. The perfumed soap composition manifests an excellent amber aroma with intense woody and earthy nuances.

EXAMPLE XIX

PREPARATION OF A DETERGENT
COMPOSITION

A total of 100 grams of a detergent (Lysine salt of n-dodecylbenzene sulfonic acid as more specifically described in U.S. Pat. No. 3,948,818, issued on Apr. 6, 1976) powder is mixed with 0.70 grams of the composition of Example XIII until a substantially homogeneous

composition is obtained. This composition has an excellent amber aroma with intense earthy and sweet woody nuances.

EXAMPLE XX

RASPBERRY FLAVOR FORMULATION

The following basic raspberry flavor formulation is produced:

Ingredient	Parts by Weight
Vanillin	2.0
Maltol	5.0
Parahydroxybenzylacetone	5.0
Alpha-ionone (10% in propylene glycol)	2.0
Ethyl butyrate	6.0
Ethyl acetate	16.0
Dimethyl sulfide	1.0
Isobutyl acetate	13.0
Acetic acid	10.0
Acetaldehyde	10.0
Propylene glycol	930.0

1-Acetyl-3,3-dimethyl-(2-propenyl)cyclohexane is added to half of the above formulation at the rate of 2.0%. The formulation with the 1-acetyl-3,3-dimethyl-(2-propenyl)cyclohexane is compared with the formulation without the 1-acetyl-3,3-dimethyl-(2-propenyl)cyclohexane at the rate of 0.01 percent (100 ppm) in water and evaluated by a bench panel.

The flavor containing the 1-acetyl-3,3-dimethyl-(2-propenyl)cyclohexane is found to have substantially sweeter aroma notes and a sweet raspberry, raspberry kernel-like and sweet aftertaste and mouthfeel missing in the basic raspberry formulation. It is the unanimous opinion of the bench panel that the chemical, 1-acetyl-3,3-dimethyl-(2-propenyl)cyclohexane rounds the flavor out and contributes to a very natural fresh aroma and taste as found in full ripe raspberries. Accordingly, the flavor with the addition of the 1-acetyl-3,3-dimethyl-(2-propenyl)cyclohexane is considered as substantially better than the flavor without 1-acetyl-3,3-dimethyl-(2-propenyl)cyclohexane.

EXAMPLE XXI

A. POWDER FLAVOR COMPOSITION

20 Grams of the flavor composition of Example XX is emulsified in a solution containing 300 gm gum acacia and 700 gm water. The emulsion is spray-dried with a Bowen Lab Model Drier utilizing 260 c.f.m. of air with an inlet temperature of 500° F., an outlet temperature of 200° F., and a wheel speed of 50,000 r.p.m.

B. SUSTAINED RELEASE FLAVOR

The following mixture is prepared:

Ingredient	Parts by Weight
Liquid Raspberry Flavor	
Composition of Example IX	20
Propylene glycol	9
Cab-O-Sil ® M-5	
(Brand of Silica produced by the	
Cabot Corporation of 125 High	
Street, Boston, Mass. 02110;	
Physical Properties:	
Surface Area: 200 m ² /gm	
Nominal particle size: 0.012 microns	
Density: 2.3 lbs/cu.ft.)	5.00

The Cab-O-Sil is dispersed in the liquid raspberry flavor composition of Example XX with vigorous stir-

ring, thereby resulting in a viscous liquid. 71 Parts by weight of the powder flavor composition of Part A, supra, is then blended into the said viscous liquid, with stirring, at 25° C for a period of 30 minutes resulting in a dry, free flowing sustained release flavor powder.

EXAMPLE XXII

10 Parts by weight of 50 Bloom pigskin gelatin is added to 90 parts by weight of water at a temperature of 150° F. The mixture is agitated until the gelatin is completely dissolved and the solution is cooled to 120° F. 20 Parts by weight of the liquid flavor composition of Example XX is added to the solution which is then homogenized to form an emulsion having particle size typically in the range of 2-5 microns. This material is kept at 120° F. under which conditions the gelatin will not jell.

Coascervation is induced by adding, slowly and uniformly 40 parts by weight of a 20% aqueous solution of sodium sulphate. During coascervation, the gelatin molecules are deposited uniformly about each oil droplet as a nucleus.

Gelation is effected by pouring the heated coascervate mixture into 1,000 parts by weight of 7% aqueous solution of sodium sulphate at 65° F. The resulting jelled coascervate may be filtered and washed with water at temperatures below the melting point of gelatin, to remove the salt.

Hardening of the filtered cake, in this example, is effected by washing with 200 parts by weight of 37% solution of formaldehyde in water. The cake is then washed to remove residual formaldehyde.

EXAMPLE XXIII

100 Parts by weight of chicle are mixed with 4 parts by weight of the flavor prepared in accordance with Example XXI 300 Parts of sucrose and 100 parts of corn syrup are added. Mixing is effected in a ribbon blender with jacketed side walls of the type manufactured by the Baker Perkins Co.

The resultant chewing gum blend is then manufactured into strips 1 inch in width and 0.1 inches in thickness. The strips are cut into lengths of 3 inches each. On chewing, the chewing gum has a pleasant long lasting raspberry flavor.

EXAMPLE XXIV

CHEWING GUM

100 Parts by weight of chicle are mixed with 18 parts by weight of the flavor prepared in accordance with Example XXII 300 Parts of sucrose and 100 parts of corn syrup are then added. Mixing is effected in a ribbon blender with jacketed side walls of the type manufactured by the Baker Perkins Co.

The resultant chewing gum blend is then manufactured into strips 1 inch in width and 0.1 inches in thickness. The strips are cut into lengths of 3 inches each. On chewing, the chewing gum has a pleasant long lasting raspberry flavor.

EXAMPLE XXV

TOOTHPASTE FORMULATION

The following separate groups of ingredients are prepared:

Parts by Weight	Ingredient
Group "A"	
30.200	Glycerin
15.325	Distilled Water
.100	Sodium Benzoate
.125	Saccharin Sodium
.400	Stannous Fluoride
Group "B"	
12.500	Calcium Carbonate
37.200	Dicalcium Phosphate (Dihydrate)
Group "C"	
2.000	Sodium N-Lauroyl Sarcosinate (foaming agent)
Group "D"	
1.200	Flavor Material of Example XXI
15 100.00 (Total)	

PROCEDURE:

1. The ingredients in Group "A" are stirred and heated in a steam jacketed kettle to 160° F.
 2. Stirring is continued for an additional three to five minutes to form a homogenous gel.
 3. The powders of Group "B" are added to the gel, while mixing until a homogenous paste is formed.
 4. With stirring, the flavor of "D" is added and lastly the sodium n-lauroyl sarcosinate.
 5. The resultant slurry is then blended for one hour. The completed paste is then transferred to a three roller mill and then homogenized, and finally tubed.
- The resulting toothpaste when used in a normal tooth-brushing procedure yields a pleasant raspberry flavor, of constant streng intensity throughout said procedure (1-1.5 minutes).

EXAMPLE XXVI

CHEWABLE VITAMIN TABLETS

The flavor material produced according to the process of Example XXII is added to a Chewable Vitamin Tablet Formulation at a rate of 10 gm/Kg which Chewable Vitamin Tablet Formulation is prepared as follows:

In a Hobart Mixer, the following materials are blended to homogeneity:

	Gms/1000 tablets
Vitamin C (ascorbic acid)	
as ascorbic acid-sodium ascorbate mixture 1:1	70.0
Vitamin B ₁ (thiamine mononitrate)	
as Rocoat ^R thiamine mononitrate 33½%	
(Hoffman La Roche)	4.0
Vitamin B ₂ (riboflavin)	
as Rocoat ^R riboflavin 33½%	5.0
Vitamin B ₆ (pyridoxine hydrochloride)	
as Rocoat ^R pyridoxine hydrochloride 33½%	4.0
Niacinamide	
as Rocoat ^R niacinamide 33½%	33.0
Calcium pantothenate	11.5
Vitamin B ₁₂ (cyanocobalamin)	
As Merck 0.1% in gelatin	3.5
Vitamin E (dl-alpha tocopheryl acetate)	
as dry Vitamin E acetate 33½% Roche	6.6
d-Biotin	0.044
Certified lake color	5.0
Flavor of Example XXII	(as indicated above)
Sweetener - sodium saccharin	1.0
Magnesium stearate lubricant	20.0
Mannitol q.s. to make	500.0

- 65 Preliminary tablets are prepared by slugging with flat-faced punches and grinding the slugs to 14 mesh. 13.5 Grams dry Vitamin A Acetate and 0.6 grams Vitamin D are then added as beadlets. The

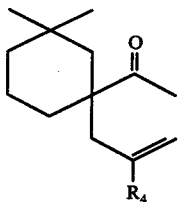
29

entire blend is then compressed using concave punches at 0.5 grams each.

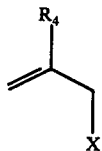
Chewing of the resultant tablets yields a pleasant, long-lasting, consistently strong raspberry flavor for a period of 12 minutes.

What is claimed is:

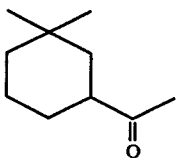
1. A process for preparing a compound having the structure:



comprising the step of reacting an allylic halide having the structure:

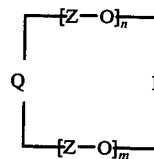


with 1-acetyl-3,3-dimethylcyclohexane having the structure:

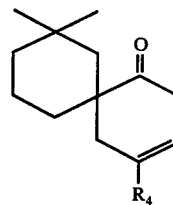


in the presence of a crown ether having the structure:

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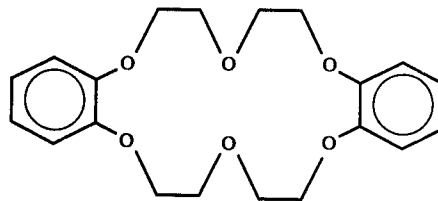


and potassium hydroxide and toluene, and heating the resulting mixture to reflux for a period of time sufficient to cause conversion to said compound having the structure:



wherein R_4 is methyl or hydrogen; X is chloro or bromo; Z is C_1 - C_4 lower alkylene; n is an integer of from 3 up to 8; p and q are the same or different and each represents C_1 - C_4 lower alkylene or orthophenylene.

2. The process of claim 1 wherein the crown ether is dibenzo-18-crown 6 having the structure:



3. The process of claim 2 wherein R_4 is methyl.

4. The process of claim 2 wherein R_4 is hydrogen.

5. The process of claim 2 wherein the mole ratio of 1-acetyl-3,3-dimethylcyclohexane: allyl halide is in the range of from 0.5:1.5 up to about 1.5:0.5.

6. The process of claim 2 wherein the mole ratio of base:allylic halide reactant in the reaction mass is in the range of from about 0.75:1 up to about 1.5:1.

* * * * *